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molecule-surfactant complexes. Both significantly impair the desired adsorption of polymeric antiredeposition agents.

The adsorption of antiredeposition agents is usually a selective process dependent on the chemical constitutions of both substrate and polymer. For example, the soil antiredeposition effect of carboxymethyl cellulose is rather limited on hydrophilic fibers such as cotton. Cellulose ethers, such as methylhydroxypropyl cellulose, are effective not only with hydrophilic fibers, but also especially with more hydrophobic fibers such as polyester. Therefore, combinations of several antiredeposition agents often must be used to ensure satisfactory results with mixed laundry. In this case the absolute amount of adsorbed substance is not the determining factor, but rather the extent to which adsorption confers hydrophilic characteristics, i.e., the change in surface characteristics relative to untreated fiber surfaces. This can be characterized by observing the resulting differences in the wetting tension with respect to pure water (cf. Eq. 1 and 2). Table 10 shows that carboxymethyl cellulose, long used as an antiredeposition agent for cotton, has no effect whatsoever on polyester. By contrast, methylhydroxypropyl cellulose causes the polyester surface to become considerably more hydrophilic. Noteworthy is the fact that the effects are retained with both detergents, albeit to a somewhat reduced extent. Only with these formulations does one observe a significant increase in the soil antiredeposition effect, as evidenced by the changes in remission. Hydroxyethyl cellulose can be regarded as a representative of numerous polymers which, though they are readily adsorbed out of an aqueous solution and are capable of showing considerable antiredeposition activity in pure water, nonetheless lose most of their effectiveness in a detergent solution as a result of competitive adsorption and displacement by surfactants.

2.5. Concluding Remarks

To simplify the theoretical treatment of the washing process, it has been necessary to treat separately each of the several phenomena involved and to isolate them from one another. In any real washing process, the various mechanisms are all at work more or less simultaneously. Thus, these mechanisms affect one another in a mutually supportive and additive way.

Investigations into the theory of washing have now made possible a rather thorough understanding of the process. Despite the complexity of the washing phenomenon and the continued presence of certain unanswered questions, these physicochemical correlations have exerted a major influence on product development.

3. Detergent Ingredients

Detergents for household and institutional use are very complex formulations containing several different types of substances. These can be categorized into the following major groups:

- surfactants
- builders
- bleaching agents
- auxiliary agents

Each individual component of a detergent has its own very specific functions in the washing process, although to some extent they have synergistic effects on one another. In addition to the above substances, certain additives are made necessary by the production process, whereas other materials are introduced to improve product appearance.

3.1. Surfactants

Surfactants constitute the most important group of detergent components, and they are present in all types of detergents. Generally, these are water-soluble surface-active agents comprised of a hydrophobic portion (usually a long alkyl chain) attached to hydrophilic or solubility-enhancing functional groups.

A surfactant can be placed in one of four classes, depending on what charge is present in the chain-carrying portion of the molecule after dissociation in aqueous solution:

- anionic surfactants
- nonionic surfactants
- cationic surfactants
- amphoteric surfactants

Table 11 provides an overview of these classes.

In general, both adsorption and wash effectiveness increase with increasing chain length. For example, ionic surfactants bearing *n*-alkyl

Table 11. Surfactants of various ionic nature [39]

Surfactant	Formula	Electrolytic dissociation	Ionic nature
Alkyl poly(ethylene glycol) ethers	$RO-(CH_2-CH_2-O)_nH$	no	nonionic
Alkylsulfonates	$R-SO_3^- Na^+$	yes	anionic
Dialkyldimethylammonium chlorides	$\left[\begin{array}{c} R \\ \\ H_3C-N^+-CH_3 \\ \\ R \end{array} \right] Cl^-$	yes	cationic
Betaines	$\begin{array}{c} CH_3 \\ \\ R-N^+-CH_2-C(=O)O^- \\ \\ CH_3 \end{array}$		amphoteric

groups show a linear relationship between the number of carbon atoms in the surfactant molecule and the logarithm of the amount of surfactant adsorbed on activated carbon or kaolin [40], [41].

The structure of the hydrophobic residue also has a significant effect on surfactant properties. Surfactants with little branching in their alkyl chains generally show good wash effectiveness but relatively poor wetting characteristics, whereas more highly branched surfactants are good wetting agents but have unsatisfactory detergency. For compounds containing an equal number of carbon atoms in their hydrophobic residues, wetting power increases markedly as the hydrophilic groups move to the center of the chain or as branching increases, but a simultaneous decrease in adsorption and washing power occurs (Figs. 27 and 28).

The changes with respect to adsorption, wetting, and wash effectiveness that result from varying the degree of branching are far more significant for ionic surfactants than for nonionic surfactants. In the case of anionic surfactants, losses in wash effectiveness caused by increased branching can be recovered to some extent, provided the overall number of carbon atoms is increased in an appropriate fashion.

Household washing of textiles normally poses few situations requiring extraordinary wetting power. If problems do arise, they can usually be overcome by increasing the wash time or the amount of detergent used. Most important is the effectiveness of the rolling-up process. Optical microscopy has revealed that oily and greasy soil tends to reside in more or less evenly distributed layers on the surface of fibers. These layers are gradually constricted by the action of a surfactant and its associated spreading pres-

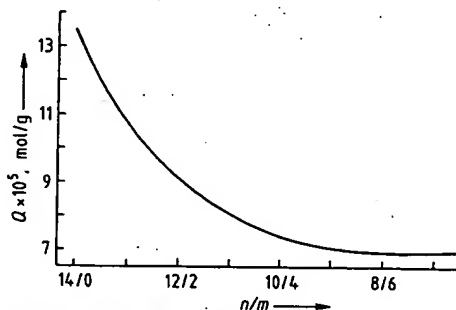
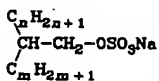


Figure 27. Decrease in adsorbed amount Q at equilibrium with increased branching of the hydrophobic residue [40]

Adsorbent: activated carbon M; amount of adsorbent: 0.050 g; particle diameter: 0.084 cm; surfactant:



surfactant concentration: 1×10^{-4} mol/L; temperature: 25°C

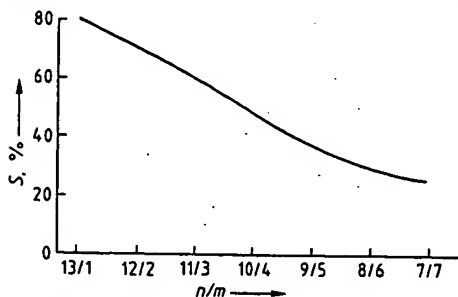
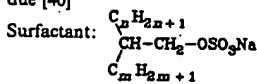


Figure 28. Decrease in soil removal S from soiled cotton as a function of increased branching in the hydrophobic residue [40]



temperature: 90°C; bath ratio: 1:12.5; water hardness: 16°d; surfactant concentration: 2.91×10^{-3} mol/L

Table 12. Key surfactants

Structure		Chemical name	Acronym
Anionic surfactants			
$R-CH_2-C(=O)ONa$	$R = C_{10-16}$	soaps	
$R-C_6H_4-SO_3Na$	$R = C_{10-13}$	alkylbenzenesulfonates	LAS
$\begin{matrix} R^1 \\ \\ R^2-CH-SO_3Na \end{matrix}$	$R^1 + R^2 = C_{11-17}$	alkanesulfonates	SAS
$H_3C-(CH_2)_m-CH=CH-(CH_2)_n-SO_3Na$ + $R-CH_2-CH(OH)-(CH_2)_x-SO_3Na$	$n + m = 9-15$ $n = 0, 1, 2, \dots \quad m = 1, 2, 3, \dots$ $R = C_{7-13} \quad x = 1, 2, 3$	α -olefinsulfonates	AOS
$\begin{matrix} R-CH-C(=O)OCH_3 \\ \\ SO_3Na \end{matrix}$	$R = C_{14-16}$	α -sulfo fatty acid methyl esters	SES
$R-CH_2-O-SO_3Na$	$R = C_{11-17}$	fatty alcohol sulfates, alkyl sulfates	FAS
$\begin{matrix} R^1 \\ \\ R^2-CH-CH_2-O-(CH_2-CH_2-O)_n-SO_3Na \end{matrix}$	a) $R^1 = H$ $R^2 = C_{10-13}$ b) $R^1 + R^2 = C_{11-13}$ $R^1 = H, C_1, C_2, \dots$ $n = 1-4$	alkyl ether sulfates a) fatty alcohol ether sulfates b) oxo alcohol ether sulfates	FES
Cationic surfactants			
$\left[\begin{matrix} R^1 & R^3 \\ & \\ N^+ & \\ & \\ R^2 & R^4 \end{matrix} \right] Cl^-$	$R^1, R^3 = C_{16-18}$ $R^2, R^4 = C_1$	quaternary ammonium compounds tetraalkylammonium chloride	QAC
Nonionic surfactants			
$\begin{matrix} R^1 \\ \\ R^2-CH-CH_2-O-(CH_2-CH_2-O)_nH \end{matrix}$	a) $R^1 = H \quad R^2 = C_8-16$ b) $R^1 + R^2 = C_{7-13}$ $R^1 = H, C_1, C_2, \dots$ $n = 3-15$	alkyl poly(ethylene glycol) ethers a) fatty alcohol poly(ethylene glycol) ethers b) oxo alcohol poly(ethylene glycol) ethers	AEO
$R-C_6H_4-O-(CH_2-CH_2-O)_nH$	$R = C_8-12 \quad n = 5-10$	alkylphenol poly(ethylene glycol) ethers	APEO
$\begin{matrix} O \\ \\ R-C-N \begin{matrix} (CH_2-CH_2-O)_nH \\ (CH_2-CH_2-O)_mH \end{matrix} \end{matrix}$	$R = C_{11-17}$ $n = 1, 2 \quad m = 0, 1$	fatty acid alkanolamides	FAA
$RO-(CH_2-CH_2-O)_n-\begin{matrix} CH_3 \\ \\ (CH_2-CH-O)_mH \end{matrix}$	$R = C_8-16$ $n = 3-8 \quad m = 3-6$	fatty alcohol polyglycol ethers (EO/PO adducts)	FEP
$H(O-CH_2-CH_2)_m-O-\begin{matrix} CH_3 \\ \\ CH-CH_2-O \\ \\ \left(\begin{matrix} CH_2 \\ \\ H_3C-CH \\ \\ O \\ \\ H(O-H_2C-CH_2)_m \end{matrix} \right)_n \end{matrix}$	$n = 2-60$ $m = 15-80$	ethylene oxide-propylene oxide block polymers	EPE
$\begin{matrix} CH_3 \\ \\ R-N \rightarrow O \\ \\ CH_3 \end{matrix}$	$R = C_{12-16}$	alkyldimethylamine oxides	

Table 12. (continued)

Structure	Chemical name	Acronym
Amphoteric surfactants		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{N}^+\text{CH}_2-\text{C}(=\text{O})\text{O}^- \\ \\ \text{CH}_3 \end{array}$	R = C ₁₂₋₁₈	alkylbetaines
$\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{N}^+(\text{CH}_2)_9-\text{SO}_3^- \\ \\ \text{CH}_3 \end{array}$	R = C ₁₂₋₁₈	alkylsulfobetaines

sure, with the layers ultimately being reduced to drops resting loosely on the fibers, which are then easily rinsed off into the wash liquor. Thus, oily residue as a fiber wetting agent is replaced by aqueous wash solution, and the process by which it occurs has come to be known as *roll-up*.

The number of types of surfactant suitable for use in detergents has increased considerably in the past 30 years. The principal criteria for judging surfactant suitability apart from performance are toxicological and ecological characteristics. Cationic and nonionic surfactants have come to play an increasingly important role along with their anionic counterparts (cf. Table 12). Despite the wide choice of possibilities, however, only a very few surfactants account for the major share of the market, partly as a result of economic factors.

Anionic surfactants are the most common agents in detergents designed for laundry, dishwashing, and general cleansing, although nonionic surfactants of the ethylene oxide adduct variety have also acquired great importance. Cationic surfactant use is largely restricted to aftertreatment aids because of the fundamental incompatibility of these materials with anionic surfactants. Amphoteric surfactants still lack a significant place in the market. Around the world a remarkable variability in the types and amounts of surfactants employed in products for similar purposes can be seen. The reasons are to be found in the variations in the kinds of fabric encountered worldwide, the diversity in washing machine technology, and different national customs for fabric use and care (Fig. 29).

Within the broad category of laundry, dishwashing, and cleansing agents, the quantity of surfactant employed is greatest for the washing of fabrics, as shown in Figure 30 for the Federal Republic of Germany.

Wash technology has been the subject of major changes and developments during the past 30 years. The textile market has also changed, with synthetic fibers playing an increasingly large role. The wide variety of substrates and their differing detergency requirements has forced manufacturers to devise surfactants with a broad spectrum of action. No single surfactant is capable of fulfilling all demands in an optimal way; consequently, the trend has been increasingly toward use of surfactant mixtures, in which the characteristics of each component are intended

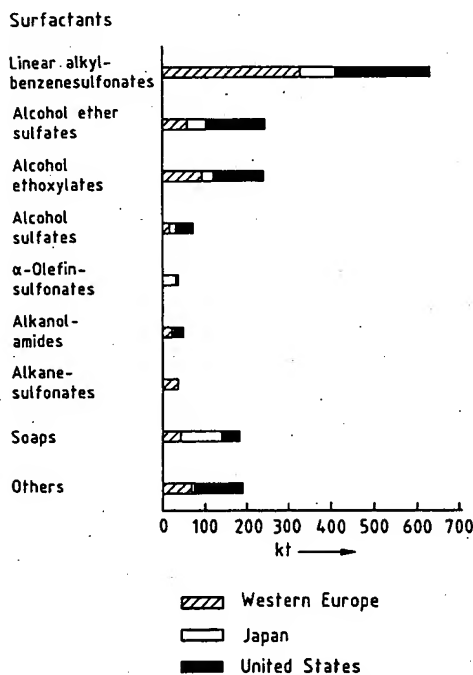


Figure 29. Household surfactant consumption, 1982 [42]

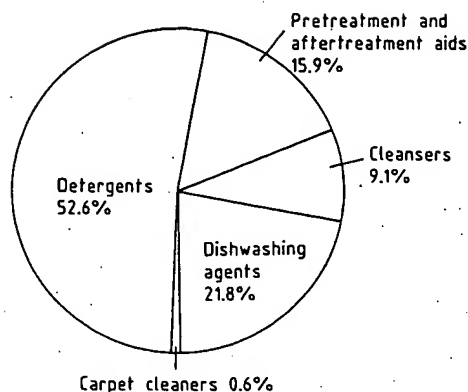


Figure 30. Distribution of surfactant consumption for various types of products in the Federal Republic of Germany [43]

to supplement those of the others. The widening scope of the demand for surfactants used in detergents not only relates to performance, but also encompasses toxicological, ecological, and economic considerations as well. A surfactant suited for detergent use is currently expected to demonstrate the following characteristics [43], [44]:

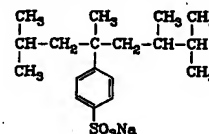
- specific adsorption
- soil removal
- low sensitivity to water hardness
- dispersion properties
- soil antiredeposition capability
- high solubility
- wetting power
- desirable foam characteristics
- neutral odor
- low intrinsic color
- storage stability
- favorable handling characteristics
- minimal toxicity to humans
- favorable environmental behavior
- assured raw material supply
- economy

3.1.1. Anionic Surfactants

Modern detergents generally contain larger amounts of anionic surfactants than nonionic surfactants. The following discussion is especially concerned with anionic surfactants that are either already widely in use or have favorable characteristics, suggesting their likely presence in various products in the future.

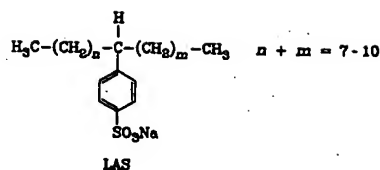
Soap. Soap is no longer as important as it was before the existence of mass-produced synthetic detergents. Although the so-called detergent soaps once contained as much as 40% soap as their sole surfactant, current powdered detergents are formulated with mixtures of far more effective surfactants in considerably smaller proportion. A further reason for the disappearance of soap from cleansing agents is its sensitivity to water hardness, manifested through inactivation due to the formation of lime soap, which tends to accumulate on fabrics and washing machine components. Such accumulation reduces the absorbency of fabrics and their permeability to air, and eventually through "aging" causes laundry to become discolored and to develop a disagreeable odor. The primary function that remains for soap currently is as a foam regulator (cf. Section 3.4.3). Nonetheless, some countries still have soap-based cleansing agents, e.g., South Korea and various African states. In addition, in the United Kingdom, one leading manufacturer still distributes a heavy-duty detergent formulated with soap.

Alkylbenzenesulfonates (ABS). Until the mid-1960s, this largest of the synthetic surfactant classes was most prominently represented by tetrapropylenebenzenesulfonate (TPS):



In the 1950s TPS had largely replaced soap as an active ingredient in detergents. It was later found, however, that the branched side-chain present in TPS prevents the compound from undergoing efficient biodegradation; thus, means were developed to replace it by more biodegradable straight-chain derivatives. Since that time, favorable economic circumstances and good performance characteristics have permitted straight-chain or linear alkylbenzenesulfonate (LAS) to take the lead among laundry detergent surfactants in Western Europe, the United States, and Japan. Nevertheless, a few countries remain in which TPS continues to be used in detergents.

Apart from its effective performance, LAS has very interesting foaming characteristics, which are of great significance to its use in detergents. Its foaming ability is high, and the foam



that is produced is readily stabilized by foam stabilizers, an important factor in the United States and Japanese markets. At the same time, however, LAS can be controlled easily by foam inhibitors, and this is significant with respect to detergents for the Western European market, where drum-type washing machines are common.

As a result of its high solubility, LAS also is employed in formulations for liquid detergents. However, LAS is sensitive to water hardness: the detergency power of LAS diminishes as the hardness of the water increases. The relationship between water hardness and performance for a series of surfactants is well demonstrated by soil removal from wool, as illustrated in Figure 31.

The decline in detergency with increasing water hardness is most dramatic with soap. Sensi-

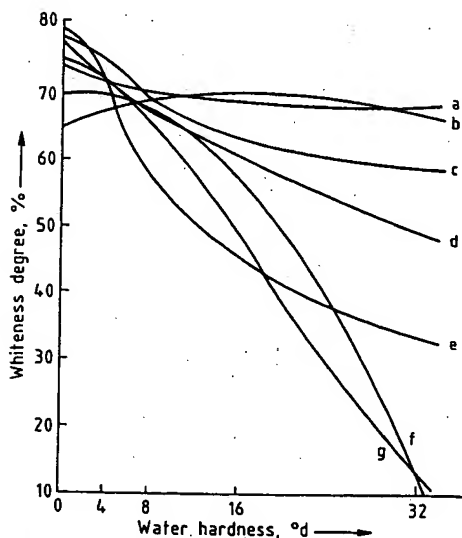


Figure 31. Detergency performance on wool by various surfactants as a function of water hardness [45]
Time: 15 min; temperature: 30 °C; bath ratio: 1:50; concentration: 0.5 g/L surfactant + 1.5 g/L sodium sulfate
a) Nonylphenol 9 EO; b) C_{12-14} Fatty alcohol 2 EO sulfates; c) C_{13-18} α -Olefin sulfonates; d) C_{16-18} α -Sulfo fatty acid esters; e) C_{12-18} Fatty alcohol sulfates; f) C_{10-13} Alkylbenzenesulfonates; g) C_{13-18} Alkanesulfonates

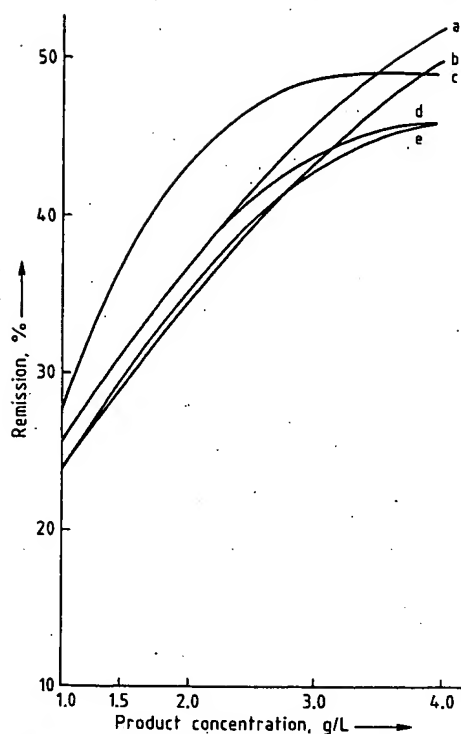
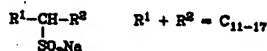


Figure 32. Detergency performance on wool of various anionic surfactants as a function of concentration [43]
Product: 25% surfactant + 75% sodium sulfate; temperature: 30 °C; wash time: 15 min; bath ratio: 1:30; water hardness: 16 °d
a) C_{12-14} Fatty alcohol 2 EO sulfates; b) C_{13-18} α -Olefin sulfonates; c) C_{16-18} α -Sulfo fatty acid esters; d) C_{13-18} Alkanesulfonates; e) Alkylbenzenesulfonates

tivity to water hardness largely disappears in phosphate- and zeolite 4A-containing formulations of the commonly used detergents because of sequestration binding or ion exchange of the hardening agents (cf. Chap. 2, Fig. 24). Figure 32 illustrates wool wash performance in water of average hardness for various readily accessible anionic surfactants in the absence of added complexing agents, plotted as a function of surfactant concentration. It can be seen that those products with a lower sensitivity to hardness display a slight advantage.

Alkanesulfonates (SAS)

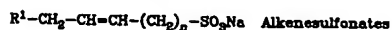


Sodium alkanesulfonates are the compounds that most nearly resemble LAS in detergency properties; therefore, these can largely be substituted for the latter in most formulations.

In contrast to alkyl sulfates, alkanesulfonates are completely insensitive to hydrolysis even at extreme pH values, a result of the presence of a direct carbon-sulfur bond.

The water hardness sensitivity and foaming characteristics of SAS resemble those of LAS as discussed above, apart from slight differences in degree.

α -Olefin sulfonates (AOS)



Olefin sulfonates are currently prepared commercially starting from α -olefins. Alkaline hydrolysis of the sultone intermediate results in ca. 60–65% alkenesulfonates and ca. 35–40% hydroxyalkanesulfonates. Because of the use of olefinic precursors, these mixtures are customarily called α -olefin sulfonates.

In contrast to LAS and SAS, AOS shows little sensitivity to water hardness (cf. Fig. 31). This apparent advantage is only of significance in a few very special applications, however. Depending on chain length, AOS can cause foaming problems in drum-type washing machines, which requires the addition of special foam inhibitors. Since this problem does not arise with washing machines of the type used in Japan, AOS has long been an important component of Japanese detergents.

In addition to the α -olefin sulfonates, sulfonates prepared from olefins with internal or central double bonds and from vinylidene olefins also exist. These types of olefin sulfonates are unsuitable for detergent use, however, because of their poor performance characteristics. In Figure 33, a C_{15-18} α -olefin sulfonate is compared with a C_{15-18} internal olefin sulfonate, the inferior performance of which is clearly apparent. The reason for the difference is the fact that AOS has its hydrophilic group in a terminal position, whereas with the internal olefin sulfonate, additional isomers can arise in which hydrophilic groups are distributed throughout the entire hy-

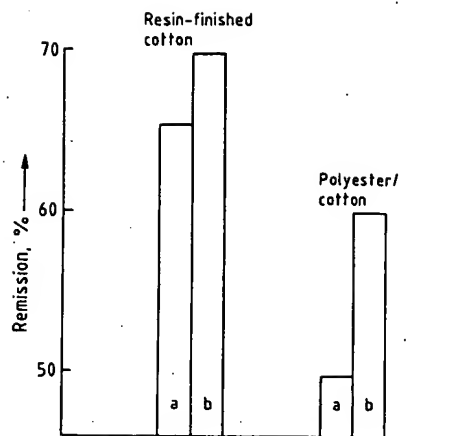
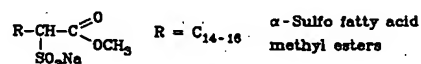


Figure 33. Performance of various olefin sulfonates [46] Water hardness: 16°d; wash time: 30 min; wash temperature: 60°C

a) 0.75 g/L C_{15-18} internal olefin sulfonates + 2.0 g/L sodium triphosphate; b) 0.75 g/L C_{15-18} α -olefin sulfonates + 2.0 g/L sodium triphosphate

drophobic chain. This has the same consequences as branching (cf. p. 339). It should be noted, however, that olefin sulfonates prepared from internal olefins generally show very good textile wetting characteristics.

α -Sulfo Fatty Acid Esters (SES)



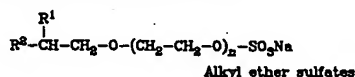
Another important class of anionic surfactants is the α -sulfo fatty acid esters, particularly the methyl derivatives. Apart from their good performance characteristics, α -sulfo fatty acid esters are distinguished by their stability, since the presence of the neighboring sulfonate group reduces any tendency toward hydrolysis of the ester function. Good detergency performance is attained only with products having rather long hydrophobic residues (e.g., stearic acid). The sensitivity of SES to water hardness is small relative to that of LAS and SAS, more nearly resembling that of AOS. One of the interesting detergency properties of α -sulfo fatty acid methyl esters is their exceptional dispersion power with respect to lime soap.

Alkyl Sulfates (FAS)



Alkyl sulfates, also known as fatty alcohol sulfates, achieved prominence as early as the 1930s in detergents for *easy care* fabrics (e.g., Fewa) and as components of textile auxiliaries. Their availability resulted from the development by SCHRAUTH of a means for preparing primary fatty alcohols by high-pressure hydrogenation of fatty acids and their methyl esters. Alkyl sulfates possess rather desirable detergency properties, and they are finding increasing application not only in specialty products, but also in heavy-duty detergents.

Alkyl Ether Sulfates (FES)



1. $R^1 = H, R^2 = C_{10-12}$ Fatty alcohol ether sulfates

2. $R^1 + R^2 = C_{11-13}$ Oxo alcohol ether sulfates

$R^1 = H, C_1, C_2 \dots$

$n = 1-4$

Alkyl ether sulfates are obtained by ethoxylation and subsequent sulfation of natural and synthetic alcohols. They exhibit the following unique characteristics relative to alkyl sulfates:

- low sensitivity to water hardness (cf. Fig. 31)
- high solubility
- storage stability at low temperature in liquid formulations

Fatty alcohol ether sulfates that are least sensitive to water hardness, e.g., sodium C_{12-14} *n*-alkyl diethylene glycol ether sulfates, actually demonstrate increased detergency performance (e.g., on wool) as the hardness increases. This is a result of the positive electrolyte effects attributable to calcium/magnesium ions. Addition of sodium sulfate produces a slight improvement only in regions of low water hardness. However, detergency performance declines in the presence of sodium triphosphate, which leads to calcium/magnesium sequestration (cf. Fig. 34).

Binding of alkaline-earth ions can occur not only through complexation, but also as a result of ion exchange. Calcium ions can be exchanged particularly effectively and with favorable kinetics through the use of zeolite 4A. The properties

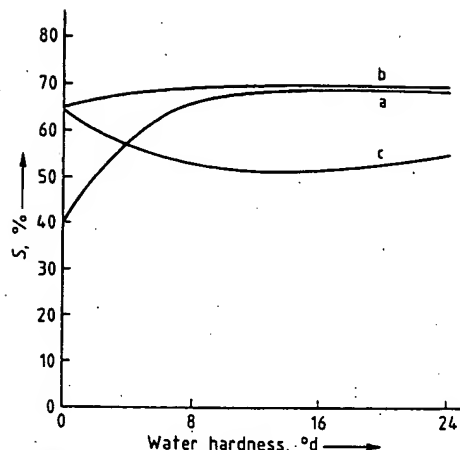


Figure 34. Soil removal *S* from wool as a function of water hardness at 30°C with 0.5 g/L sodium C_{12-14} *n*-alkyl diethylene glycol ether sulfates containing no added electrolyte (a), with 1.5 g/L sodium sulfate (b), and with 1.5 g/L sodium triphosphate (c) [7]

discussed above in the context of calcium sequestration can be equally well described in terms of ion exchange.

From the foregoing, it follows that if one were to undertake the development of, for example, a wool detergent, an important consideration would be the careful choice of supplemental salts; i.e., the presence of complexing agents or ion exchangers is not always advantageous in a detergent formulation containing surfactants if these happen to be insensitive to water hardness. On the other hand, a surfactant that is sensitive to water hardness is not necessarily inferior, provided it is combined with the proper complexing agents or ion exchangers. The situation can be somewhat more complicated, however, if one proposes to develop a detergent for fibers whose nature requires the presence of complexing agents for proper washing.

Alkyl ether sulfates are very intensively foaming compounds that are well suited to use in highly foaming detergents for agitator-type washing machines, but are less directly applicable to detergents for drum-type machines. Because of their specific properties, alkyl ether sulfates are preferred constituents of easy care and wool detergents, as well as foam baths, hair shampoos, and manual dishwashing agents. The optimal carbon chain length has been established to be C_{12-14} with ca. 2 mol of ethylene oxide.

Analogous to the alkyl sulfates, alkyl ether sulfates have achieved some importance in the United States and Japanese markets. This is because their critical micelle concentration is considerably lower than that for LAS, resulting in very satisfactory washing power even at the low detergent concentrations typical in the United States. In Europe, alkyl ether sulfate use has so far been restricted largely to specialty detergents.

Alkyl ether sulfates were formerly prepared exclusively by ethoxylation and sulfation of natural fatty alcohols. However, synthetic alcohols are also currently employed, particularly the partially branched oxo alcohols and the Ziegler alcohols. The latter are always unbranched due to their mode of synthesis and, thus, show properties largely identical with those of the natural alcohols.

3.1.2. Nonionic Surfactants

Nonionic surfactants of the alkyl polyglycol ether type do not dissociate in aqueous solution, and certain of their properties can be singled out for special attention:

- the absence of electrostatic interactions
- behavior with respect to electrolytes
- the possibility of favorable adjustment of hydrophilic-hydrophobic parameters
- anomalous solubility

Adsorption phenomena involving nonionic surfactants can be explained on the basis of hydrophobic interactions, in some cases coupled with steric effects. Electrolytes have no direct influence on adsorption with nonionic surfactants. Nonionic surfactant wash effectiveness is reduced by addition of polyvalent cations, but the cause is reduced negative ζ -potentials of substrate and soil, leading to reduced repulsion and correspondingly poor soil removal [47], [48].

An important advantage of nonionic surfactants that are based on poly(alkylene glycol) ethers as compared to ionic compounds is the fact that a proper relationship can be achieved easily between the hydrophobic and hydrophilic portions of the nonionic surfactants. For example, the hydrophilic portion of the molecule can be extended gradually by stepwise addition of ethylene oxide groups. This leads to stepwise increases in hydration and corresponding successive increases in solubility. On the other hand, with ionic surfactants, the presence of even one

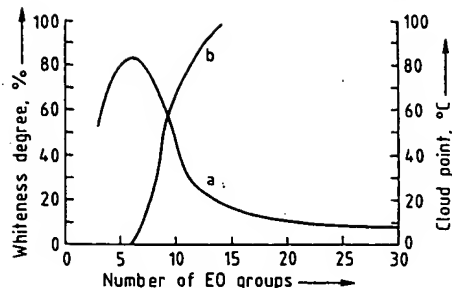


Figure 35. Detergency performance on wool and cloud point of C_{13-15} oxo alcohols as a function of degree of ethoxylation [43]

a) Wool detergency performance (temperature: 30°C; water hardness: 16°d; bath ratio: 1:30; time: 15 min; concentration: 0.75 g/L surfactant + 2.25 g/L sodium sulfate);
b) Cloud point (surfactant concentration 10 g/L)

ionic group makes such a strong contribution to hydrophilic character that the introduction of further such groups totally eliminates the possibility of any equilibrium relationship with respect to the hydrophobic portion. The result is a rapid decline in detergency properties. For a substance bearing two strong ionic hydrophilic groups to show washing activity, a considerably longer alkyl chain ($>C_{20}$) is generally necessary.

Nonionic surfactants with a given hydrophobic residue can be adjusted to show optimal properties for various substrates with respect to adsorption and wash effectiveness simply by changing the degree of ethoxylation. Wash effectiveness shows an initial increase with an increasing degree of ethoxylation, but a point is then reached after which the wash effectiveness declines markedly (Fig. 35). Textile wetting power often decreases only at very high degrees of ethoxylation, whereas the wetting power for hard hydrophobic surfaces continues to climb as the number of ethoxy groups increases.

Nonionic surfactants based on poly(alkylene glycol) ether show a solubility anomaly: when they are heated in aqueous solution, turbidity appears, usually at a relatively precise temperature. The result is a separation into two phases, one with a high water content and one with a low water content. The corresponding characteristic temperature for a given surfactant is known as its cloud point. The cloud point moves to a higher temperature as the number of ethoxy groups increases. If the cloud point is not greatly exceeded, then the largely aqueous phases and largely surfactant phases form an emulsion. For

Table 13. Detergency performance (in % remission) of alcohol ethoxylates with comparable cloud points [45]

Surfactant *	Cloud point, °C	Cotton		Resin-finished cotton		Polyester/cotton	
		60°C	90°C	60°C	90°C	60°C	90°C
C ₁₁₋₁₅ sec-Alcohol 9 EO	59	71	53	69	55	65	48
C ₉₋₁₁ Oxo alcohol 7 EO	61	57	44	66	52	53	43
Oleyl/cetyl alcohol 10 EO **	89	60	68	70	72	57	67
C ₁₃₋₁₅ Oxo alcohol 11 EO	88	54	69	67	69	53	58

* Surfactant concentration: 0.75 g/L; water hardness: 16°d; wash time: 30 min. ** Iodine number 45.

a given surfactant, adsorption (thus, washing power) decreases when the cloud point is surpassed to a significant extent. The main reason for this behavior is the diminished solubility of the washing active homologues, which are then expelled from the aqueous phase. Nevertheless, nonionic surfactants with a cloud point somewhat below the application temperature commonly show better performance than those whose cloud point is higher (Fig. 35). Thus, the application temperature is a significant factor in determining an optimal degree of ethoxylation (Table 13). The table shows that the best detergency performance is obtained when the temperature is maintained near the cloud point.

The cloud point can be greatly reduced by addition of several grams of electrolytes per liter, depending on the surfactant. It must be emphasized, however, that everything said in this section is strictly applicable only to systems comprised of pure nonionic surfactants. For binary mixtures of nonionic and ionic surfactants, it is important to recognize that even a small amount of ionic surfactant can cause the cloud point to rise more or less dramatically.

The share of nonionic surfactants in overall surfactant production has been increasing for a number of years. The major contributors to this increase have been fatty alcohol, oxo alcohol, secondary alcohol, and alkylphenol ethoxylates, all of which are obtained by reaction of the corresponding hydroxy compounds with ethylene oxide.

The reasons for the increased use of nonionic surfactants are found in their favorable detergency properties, particularly with respect to synthetics and at the decreasing wash temperatures dictated by energy conservation measures in Western Europe and the United States.

Favorable detergency properties of nonionic surfactants derive largely from the following factors:

Table 14. Critical micelle concentration c_M of various surfactants [45]

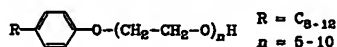
Surfactant	c_M , g/L
LAS (C ₁₀₋₁₃ alkyl)	0.65
C ₁₂₋₁₇ Alkanesulfonates	0.35
C ₁₅₋₁₈ α -Olefinsulfonates	0.30
C ₁₂₋₁₄ Fatty alcohol 2 EO sulfates	0.30
Nonylphenol 9 EO	0.049
Oleyl/cetyl alcohol 10 EO *	0.035

* Iodine number 45.

low critical micelle concentration (c_M)
very good detergency performance
soil antiredeposition characteristics with synthetic fibers

The low c_M values of nonionic surfactants mean that they display high detergency performance even at relatively low concentrations. Table 14 provides data illustrating the low c_M of these compounds relative to that of anionic surfactants.

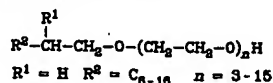
Alkylphenol Polyglycol Ethers (APEO). Alkylphenol polyglycol ethers based on octyl-, nonyl-, and dodecylphenol poly(ethylene glycol) ethers achieved early success due to their exceptional detergency properties, particularly their oil and fat removal characteristics.



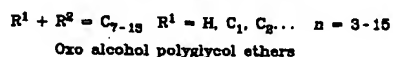
The significance of APEOs has greatly declined, however, especially in the Federal Republic of Germany, due to a debate over their environmental characteristics, particularly the extent of their biodegradability and the fish toxicity of certain metabolites resulting from partial biodegradation.

Alkyl Polyglycol Ethers (AEO). Alkyl polyglycol ethers based on natural and synthetic

(e.g., oxo or Ziegler) alcohols have become standard components of modern detergents, present to greater or lesser extent in practically all detergent formulations.

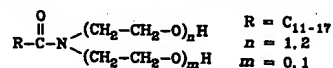


Fatty alcohol polyglycol ethers



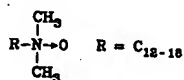
One or more ethylene oxide groups can also be replaced by propylene oxide residues. Such a change can increase the hydrophobic character of the alkyl group and permit modification of foam characteristics.

Fatty Acid Alkanolamides (FAA). Important fatty acid alkanolamides are ethanolamides of fatty acids with the following structure:



Their most important function is to act as foam boosters, adding desired stability to the foam produced by detergents prone to heavy foaming. This property is no longer desirable for the drum-type washing machines employed in Western Europe. Nevertheless, compounds in this class have taken on new meaning even in Western Europe, where they are employed as detergency boosters, particularly in low-temperature applications. A small amount of such material is capable of enhancing the soil removal properties of the classical detergent components.

Amine Oxides. The amine oxides produced by oxidation of tertiary amines with hydrogen peroxide are compounds that exhibit cationic behavior in acidic conditions (pH < 3), but they behave as nonionic surfactants under neutral or alkaline conditions. For this reason they are included in the nonionic surfactant category.



Compounds in this class have been known since 1934 and were described as detergent components in a patent issued to IG-Farbenfabriken [49]. Combinations of alkylbenzenesulfonates and specific amine oxides are reputed to be especially gentle to the skin. Despite good detergency

properties, however, the compounds are found almost exclusively in specialty detergents. The reasons for this include high cost, low thermal stability, and high foam stability.

3.1.3. Cationic Surfactants

Long-chain cationic surfactants such as distearyldimethylammonium chloride (DSDMAC) exhibit extraordinarily high sorption power with respect to a wide variety of surfaces [50]–[53]. Figure 36 shows this behavior in the case of several textile fibers. Adsorption rises steeply at low surfactant concentrations, followed by rapid saturation as the concentration increases. This behavior suggests complete coverage of boundary surfaces.

At the same time, cationic surfactants display behavior opposite that of anionic surfactants as regards charge relationships on solids. Since the surfactant molecules bear a positive charge, their adsorption reduces the negative ζ -potential of solids present in aqueous solution, thereby reducing mutual repulsions, including that between soil and fibers. Use of higher surfactant concentrations causes charge reversal; thus, sol-

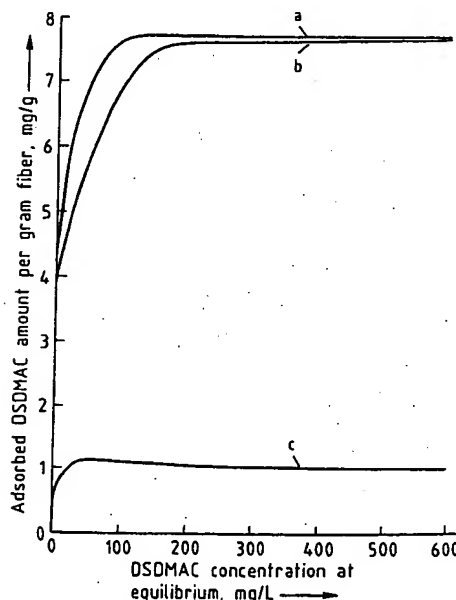


Figure 36. Adsorption isotherms of distearyldimethylammonium chloride (DSDMAC) on wool (a), cotton (b), and polyacrylonitrile (c) [50]
Temperature: 23°C; time: 20 min; bath ratio: 1:10

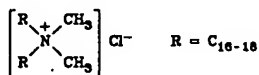
id particles become positively charged, resulting again in repulsion. Soil removal can be achieved, if adequate amounts of cationic surfactants are present and if their alkyl chains are somewhat longer than those of comparable anionic surfactants. This fact has little practical significance, however, since the subsequent rinse and dilution processes cause charge reversal in the direction of negative ζ -potentials, whereby a large fraction of the previously removed soil is once more attracted to the fibers. Therefore, cationic surfactants are employed in laundry and cleansing agents only for the purpose of achieving certain special effects, which include applications in fabric softeners, antistatic agents, and microbicides.

Mixtures made up of equivalent amounts of anionic surfactant and cationic surfactant remain virtually unadsorbed on surfaces and thus display no washing effect. Reactions between anionic and cationic surfactants produce neutral salts with extremely low water solubility. Regarding washing, these behave like an additional burden of greasy soil. On the other hand, addition of small amounts of certain specific cationic surfactants to an anionic surfactant —

or even a nonionic surfactant — can enhance detergency performance.

Nonionic surfactants are more tolerant of the presence of cationic surfactants. Mixtures of the two are sometimes used in specialty detergents intended to have a fabric softening effect. In such cases, one must take into account the fact that adsorption of the cationic surfactant can be greatly reduced by the presence of the nonionic surfactant, depending on the concentration of the latter, a phenomenon that can have a negative influence on the fabric softening characteristics (Fig. 37).

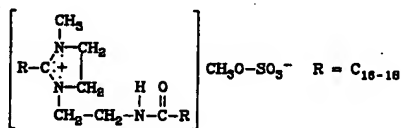
Dialkyldimethylammonium Chlorides. The first surfactant developed in this category was distearyldimethylammonium chloride (DSDMAC), introduced in 1949 as a fabric softener for diapers and presented to the United States market a year later in its present form as a laundry rinse fabric softener.



Only in the mid-1960s did these surfactants begin to have a major impact as laundry after-treatment aids on the United States and Western European markets (especially in the Federal Republic of Germany).

A recent application for DSDMAC, albeit a minor one, is as a wash cycle fabric softener in specialty detergents.

Imidazolinium Salts. Imidazolinium salts of the type 1-(alkylamidoethyl)-2-alkyl-3-methylimidazolinium methyl sulfate have achieved a place as rinse softening agents, although not nearly as significant as that of DSDMAC.



Alkyldimethylbenzylammonium Chlorides. Compounds of the alkyldimethylbenzylammonium chloride type show only limited fabric softening character, but they are used in laundry disinfecting agents as a result of their activity toward gram-positive and gram-negative bacteria.

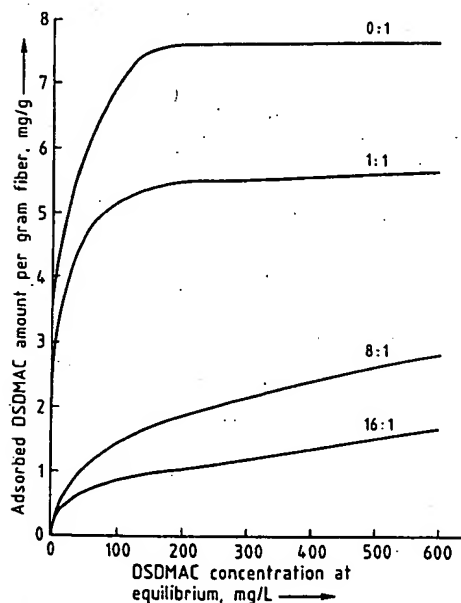
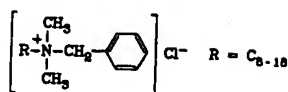


Figure 37. Adsorption isotherms of distearyldimethylammonium chloride (DSDMAC) on cotton as a function of the alkyl polyglycol ether:DSDMAC ratio at equilibrium [50]

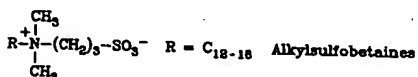
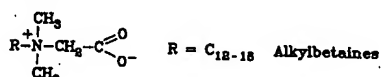
Temperature: 23°C; time: 20 min; bath ratio: 1:10



The high adsorption capability of alkyl-dimethylbenzylammonium chloride also leads to applications as antistatic agents in laundry after-treatment products.

3.1.4. Amphoteric Surfactants

Compounds of the alkylbetaine or alkylsulfobetaine type possess both anionic and cationic groups in the same molecule even in aqueous solution. Despite what could be seen in some respects as excellent detergency properties, these substances are only rarely employed in specialty detergents, the reasons being primarily economic.



3.2. Builders

Detergent builders play a central role in the course of the washing process [54], [55]. Their function is largely that of supporting detergent action and of eliminating calcium and magnesium ions, which arise partly from the water and sometimes also from soil and fabrics.

The category of builders is comprised of several types of materials: specific alkaline substances such as sodium carbonate and sodium silicate; complexing agents like sodium diphosphate-sodium triphosphate or nitrilotriacetic acid (NTA); and ion exchangers, such as water-soluble polycarboxylic acids and insoluble zeolites (e.g., zeolite 4A).

Modern detergent builders must fulfill a number of criteria [7]:

- 1) Elimination of alkaline-earth ions from water, textiles, soil
- 2) Single wash cycle performance
 - high specific detergency for pigments and fats
 - distinct detergency on specific textile fibers

enhancement of surfactant properties
dispersion of soil in detergent solutions
favorable influence on foam characteristics

- 3) Multiple wash cycle performance
 - good soil antiredeposition capability
 - prevention of incrustations on textiles
 - prevention of deposits in washing machines
 - favorable anticorrosion properties
- 4) Commercial properties
 - chemical stability
 - industrial handleability
 - no hygroscopic tendencies
 - optimal color and odor qualities
 - compatibility with other detergent ingredients
 - storage stability
 - assured raw material basis
- 5) Human toxicological safety assurance
- 6) Environmental properties
 - response to deactivation by biological degradation, adsorption, or other mechanisms
 - no negative influence on the biological systems found in sewage plants and surface water
 - no uncontrolled accumulation
 - no heavy-metal remobilization
 - no eutrophication
 - no detrimental effects on drinking water quality
- 7) Economy

3.2.1. Alkalies

Alkalies such as potash and soda have been used to enhance the washing effectiveness of water since antiquity. Their activity is based on the fact that soil and fibers become more negatively charged as the pH increases, resulting in increased mutual repulsion. Alkali also precipitates ions that contribute to water hardness.

At the beginning of the 20th century, the principal ingredients (apart from soap) of all detergents were soda and silicate, which often comprised nearly 50% of the formulation of a powdered detergent. These substances were somewhat replaced during the 1930s by sodium monophosphate, and currently, at least in Western Europe, a household detergent that contained only soda or monophosphate as builders would be classed as outmoded. Modern builders